AEROMMA:
Atmospheric Emissions and Reactions
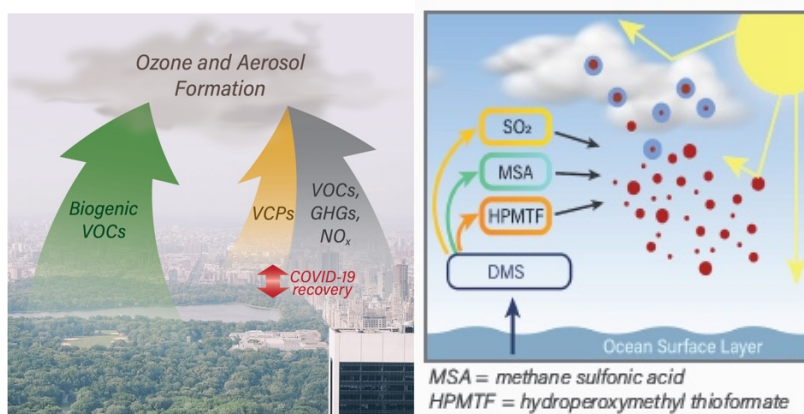Observed from Megacities to Marine Areas



A comprehensive study led by NOAA's Chemical Sciences Laboratory investigating anthropogenic and marine emissions that alter tropospheric composition and impact air quality and climate



MSA = methane sulfonic acid
HPMTF = hydroperoxymethyl thioformate

# Atmospheric Emissions and Reactions Observed from Megacities to Marine Areas (AEROMMA 2021)

*NOAA Chemical Sciences Laboratory*

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## Statement of Opportunity

Over half of the world's population lives in cities, and the number is anticipated to grow in all regions [*UN*, 2018]. Cities are estimated to account for ~70% of the global fossil carbon dioxide ($CO_2$) emissions [*Duren and Miller*, 2012], and $CO_2$ is the largest positive forcing on global climate [*IPCC*, 2018]. Air pollution is the fifth largest human health risk factor globally [*Gakidou et al.*, 2017], and a public health concern in megacities around the world.

Oceans cover ~70% of the surface area of the globe and impact climate, including through the emissions of dimethyl sulfide (DMS) from phytoplankton. DMS oxidizes in the marine atmosphere to form sulfate aerosol, which can serve as cloud condensation nuclei (CCN) [*Andreae*, 1990]. Many of the U.S.'s largest cities are located on or near coastlines, providing an opportunity to assess interactions of anthropogenic and marine emissions, and atmospheric chemistry affecting both climate and air quality.

Recent research from the NOAA Chemical Sciences Laboratory (CSL) reveal major gaps in our understanding of both urban and marine chemistry. In urban atmospheres, volatile chemical products (VCPs = coatings, adhesives, inks, personal care products, cleaning agents, etc.) are emerging as a major source of volatile organic compounds (VOCs) [*McDonald et al.*, 2018a]. The emissions and impacts of VCPs on atmospheric chemistry are not well understood. In the presence of nitrogen oxides ($NO_x$), VOCs undergo chemistry that lead to the formation of ground-level ozone and aerosols. In a pilot study performed in conjunction with the Long Island Sound Tropospheric Ozone Study (LISTOS), NOAA CSL field measurements in New York City revealed that fragranced consumer products and other VCPs account for over half of the anthropogenic VOC emissions, and enhance formation of ground-level ozone during a heatwave event [*Coggon et al.*, 2020]. While VCPs emissions are included in the US National Emissions Inventory (NEI), and have been regulated for their impacts on ozone formation and air toxics [*EPA*, 1995], their emissions may be underestimated by a factor of 2-3 [*McDonald et al.*, 2018a]. Over time the composition of VCPs has changed, shifting away from aromatics and chlorinated solvents towards oxygenated VOCs with the inclusion of fragranced components like d-limonene [*Weschler*, 2009].

After decades of decline in ground-level ozone and fine particulate matter ($PM_{2.5}$), the downward trends may be slowing in the most recent years (https://www.epa.gov/air-trends). This could be a result of unanticipated trends in emissions [*Jiang et al.*, 2018; *McDonald et al.*, 2018a], increasing influence of regional background sources [*Silvern et al.*, 2019], long-range transport [*Owen R. Cooper et al.*, 2015], changes in atmospheric chemistry [*Laughner and Cohen*, 2019], and/or a consequence of a changing climate with heatwaves in the US becoming more frequent,

longer in duration, and more intense [*Habeeb et al.*, 2015]. Many US metropolitan areas violate the 8-hour ozone standard as regulated under the Clean Air Act, which is of concern to environmental managers. In addition to air quality, many cities and states are developing plans to reduce their carbon footprint, including for $CO_2$ and methane ($CH_4$). Such efforts will impact future emissions of VOCs and $NO_x$ with potential co-benefits on air quality.

Biogenic sulfur oxidation products, mainly from oceanic DMS ($CH_3SCH_3$) emissions, are the primary driver of particulate sulfur formation in the remote atmosphere. The DMS oxidation mechanism is not fully characterized, and many of the key intermediates affecting aerosol and sulfur dioxide ($SO_2$) yields have only been theorized. Accurate representation of both the DMS oxidation product branching fractions and timescales in chemical transport models is critical to establishing a quantitative relationship between oceanic DMS emissions and atmospheric particle number and CCN concentrations in the marine boundary layer (MBL). Recent developments in the understanding of this system, mainly the discovery of hydroperoxymethyl thioformate [*Veres et al.*, 2019] (HPMTF, Fig. 1), highlight the degree to which global models inaccurately parameterize this chemistry. These recent advances motivate a reexamination of several decades of research assessing the role of DMS derived CCN relative to other sources of marine CCN, such as sea-spray aerosol, long-range transport of terrestrial particles, and secondary marine aerosol produced from non-DMS precursors [*O'Dowd and De Leeuw*, 2007; *Prather et al.*, 2013; *Quinn and Bates*, 2011], in both pre-industrial and present-day atmospheres [*Carslaw et al.*, 2013].

To improve our understanding of emissions and chemical reactions that affect climate and air quality, the NOAA Chemical Sciences Laboratory proposes the **A**tmospheric **E**missions and **R**eactions **O**bserved from **M**egacities to **M**arine **A**reas (AEROMMA) field campaign to collect new observations from megacities to marine environments. The largest US cities are on coasts (e.g., Los Angeles and New York City), which allows for assessments of the interactions between megacity and marine environments. The chemical instrumentation that will be used on theWP-3 NOAA aircraft will address gaps in both urban and marine chemistry. It is anticipated that the field observations will:

(1)     Provision of timely information to environmental managers and stakeholder groups on emissions from VCPs and fossil fuel sources that impact climate and air quality;

(2)     Assessment of emissions recovery following the COVID-19 pandemic;

(3)     Reduce of uncertainties in global climate models due to marine aerosols from biogenic sulfur emissions;

(4)     Provision of urban and marine datasets to improve the representation of emissions and chemical and physical processes in the next generation NOAA weather-chemistry models.

Both major science questions, on VCPs and biogenic sulfur, are current "hot topics" in the atmospheric science community that NOAA CSL has initiated with prior research. Due to our position at the forefront of this research, NOAA CSL, its collaborators, and stakeholders have an unparalleled opportunity to lead in the efforts to (1) refine understanding of the biogenic sulfur oxidation system and elucidate its impacts on Earth's radiative budget and to (2) improve urban

emission inventories to assess their influence on trends of ozone and aerosol precursors, as well as (3) quantifying associated co-benefits between air quality and greenhouse gases.

## Major Science Objectives and Questions:

*Emissions, air quality, and climate in urban areas*

(A) AEROMMA2021 will determine **organics emissions and chemistry**, including of understudied VCPs in the most populated urban areas in the United States, to better understand the impact on ozone and aerosol formation, and to study their relative importance on urban air quality compared to other sources of VOCs such as from energy-related, cooking, and biogenic sources.

1. How well do **current emission inventories** quantify the flux of anthropogenic VOC emissions over North American cities, including VCPs, mobile sources, cooking, and industrial facilities?

2. How does the relative **distribution of VOC emissions** vary by city and population density, influencing the ratio of VCP to mobile source emissions?

3. What **chemical tracers** can be used to source apportion VOCs amongst VCPs, energy-related, cooking, and biogenic sources?

4. How have **VOC emissions changed** between AEROMMA2021 and previous urban measurements (e.g., NEAQS2002, ICARTT2004, TEXAQS2006, CalNex2010, SENEX2013, WINTER2015, NY-ICE/LISTOS2018, FIREX-AQ2019, etc.)?

5. What is the **composition of gas- and aerosol phase organics in the urban atmosphere**, including aromatics, alkanes, terpenes, cycloalkanes, oxygenated VOCs (including water-soluble organics such as alcohols, esters, glycols, and glycol ethers), and organic aerosol?

6. How do **understudied oxygenated VOCs from VCPs** and their oxidation products affect atmospheric oxidant budgets, and how well do models represent oxygenated VOC chemistry, including heterogeneous reactions?

7. What is the relative role of **anthropogenic versus biogenic VOCs** on ozone and organic matter formation, and how does this vary between vegetated and non-vegetated regions?

8. What is the **formation rate of ozone and particulate matter** in urban outflow, and to what extent do non-traditional sources (e.g., VCPs and cooking) affect the amount of ozone and aerosols formed?

9. How do organics affect the evolution of **particle size, number distribution, and aerosol optical properties (e.g., brown carbon)** in urban outflow, and to what extent does urban outflow contribute to cloud condensation nuclei (CCN) formation?

(B) Determine **reactive nitrogen emissions and chemistry** in major urban corridors (i.e., urban core to suburban and outlying rural areas) to understand the current importance of combustion and non-combustion sources, continue the trend analysis and determine changes in the reactive nitrogen cycle chemistry and its influence on ozone and aerosol formation.

1. How well do **current emission inventories** quantify the flux of anthropogenic nitrogen oxides ($NO_x = NO + NO_2$) over North American cities, including from mobile sources, buildings, industrial facilities, and outlying agricultural regions and power generation?

2. How have **$NO_x$ emissions changed** between AEROMMA2021 and previous urban measurements (e.g., NEAQS2002, ICARTT2004, TEXAQS2006, CalNex2010, SENEX2013, WINTER2015, NY-ICE/LISTOS2018, FIREX-AQ2019, etc.)?

3. How does the $NO_x$ lifetime affect the interpretation of satellite retrievals of nitrogen dioxide ($NO_2$) as a **constraint on urban to rural $NO_x$** emission inventories?

4. What is the **relative role of combustion** (e.g., mobile sources) versus non-combustion sources (e.g., agricultural soils and VCPs) of $NO_x$, nitrous acid (HONO), ammonia ($NH_3$), and VOCs on ozone and ammonium nitrate formation?

5. How do the formation rates of ozone and particulate matter in urban outflow evolve from **high to low $NO_x$ regions**?

6. What is the speciation of oxidized reactive nitrogen in urban outflow in 2021, and does it differ substantially from previous campaigns due to evolving $NO_x$-VOC chemistry due to changes in dominant emission sources?

(C) Determine the fraction of urban VOC and $NO_x$ emissions associated with emissions of $CO_2$ and methane ($CH_4$) from transportation, buildings, industry, and landfills to quantify **co-benefits between managing air quality and the carbon cycle**.

1. How well do **current emission inventories** quantify the flux of anthropogenic $CO_2$ and $CH_4$ emissions over North American cities, including from mobile sources, buildings, industrial facilities, natural gas infrastructure, and landfills?

2. How does the flux of **$CO_2$ and $CH_4$ emissions vary between North American cities**, including as a function of population density and age of energy infrastructure?

(D) Investigate urban and coastal meteorology, to better understand **extreme heat** on urban air quality, **urban heat islands**, and the role of **long-range transport** versus local sources of air pollution.

1. How does **extreme heat** affect urban and coastal meteorology, photochemistry, and ozone and aerosol formation?

2. How does the **urban canopy affect** urban heat islands, land-sea breezes, and planetary boundary layer (PBL) dynamics?

3. What is the **local versus regionally- and continentally-transported contributions** to ozone, and how is the relative contribution affected by **heatwaves**?

(E) Assess how the emissions in U.S. urban areas recover after the COVID-19 outbreak and economic crisis during which the emissions and urban air quality have changed due to decreased traffic and economic activities.

1. How have **emissions recovered** after the decrease in economic activities during COVID-19?

2. Have the distribution and magnitude of VCP, mobile source, and industrial emissions changed; **is there a new normal after COVID-19**?

3. Are there **differences in chemistry** leading to ozone and secondary $PM_{2.5}$ compared to the lower emission and different VOC/NOx ratios measured during the NOAA COVID-AQS 2020 campaign?

## *Investigating the interface of urban and marine atmosphere*

(A) AEROMMA2021 will provide observations at the interface of the marine atmosphere and the urban airshed to quantify what impact marine emissions have on urban air quality and composition and the impact of urban outflow on marine chemistry. Observations will resolve the relative contributions to $SO_2$, sulfate aerosols, and CCN from biogenic and anthropogenic sulfur sources.

1. What are the relative contributions of urban, ship emissions, secondary marine production to the **$SO_2$ budget**?

2. How does anthropogenic **NOx impact oxidation of sulfur** and the distribution of secondary species in the marine atmosphere?

3. What impacts do **marine halogens** have on the atmospheric oxidant budget through the photolysis of key marine species, e.g. $ClNO_2$, $Cl_2$, and BrO?

4. Are marine gases important factors for **ozone formation in coastal urban regions**?

5. Where is the transition from **isomerization chemistry forming HPMTF** to bimolecular NO chemistry forming $SO_2$?

(B) Utilize observations of aerosol abundance and composition to understand the impact of the various sources of biogenic and anthropogenic emissions on aerosol and CCN formation.

1. What fractions of **CCN producing aerosol** is natural versus controlled by anthropogenic emissions?

2. How well do **regional and global models** predict the influence of urban and marine secondary aerosols on climate?

3. How will the distribution of aerosols and **CCN sources change in the future** as a result of Earth's warming and changes in anthropogenic emissions?

4. Does the **mixing of urban and marine aerosols** impact SOA formation and the atmospheric fate of aerosols?

*Investigation of the remote marine atmosphere*

AEROMMA2021 will exploit the range and capabilities of the NOAA WP-3D to sample the remote marine atmosphere in regions with (1) limited impacts from anthropogenic sources, (2) high atmospheric burden from biogenic emission, (3) stable meteorology, and (4) a well-defined marine boundary layer.

(A) Investigation of the emissions and chemistry in the remote marine atmosphere that drive the formation of secondary products and marine aerosols. Flux observations will be used to better quantify the air-sea exchange of VOCs to better understand the atmospheric budget of gas-phase precursor species in the remote atmosphere.

1. What are the sources of VOCs and **volatile sulfur in the remote marine atmosphere**?

2. How well do we understand the **net oceanic flux of biogenic sulfur**?

3. How do primary oceanic **emissions of sea spray** impact the marine aerosol burden, spatial distribution and properties?

4. At what rates are atmospheric gases and aerosol **deposited to the ocean's surface**?

(B) Observations to better characterize the marine sulfur oxidation cycle and secondary aerosol formation and dependencies on key parameters such as temperature, $NO_x$, and background aerosol.

1. How well do we understand **oxidation of biogenic sulfur** and VOCs in the remote marine atmosphere?

2. How does the oxidation of biogenic marine emissions couple to **aerosol production and growth**?

3. What are the processes that drive the **removal of secondary gases** and aerosols throughout marine boundary layer?

4.  How will the **products form the oxidation of DMS be** impacted by changes in temperature as a result of changes in Earth's climate?

(C) Utilize measurements throughout the marine boundary layer in both clouded and cloud-free conditions to quantify air-sea exchange of trace gases and production of primary aerosol, and aqueous aerosol and cloud scavenging. We aim to better identify the linkages between marine emissions and aerosol abundance to improve predictions of marine aerosol-cloud-climate interactions in a changing climate. This data set will be valuable for evaluating models identifying the impact of a changing climate on CCN sources, cloud albedo and Earth's radiative budget.

1.  What fraction of the organic aerosol is **primary versus secondary** at various time scales?

2.  How well do **current models** represent primary and secondary marine aerosols and their radiative properties, and what are the largest associated uncertainties?

3.  How important is the formation of secondary aerosol from **aqueous-phase processes**?

4.  How do **aerosol optical properties** evolve due to secondary production and particle phase transitions?

5.  What are the sources of **new particles in the remote troposphere**, how rapidly do they grow to CCN-active sizes, and how well are these processes represented in CCMs?

**Motivation**

_**North American Megacity VOC Emissions, Chemistry, and Trends**_

Volatile organic compounds (VOCs) emitted into the urban atmosphere are one of the needed ingredients for ozone and aerosol formation and therefore have the potential to impact air quality. For decades, fossil fuel usage has been considered to be the primary source of urban VOCs in megacities around the world, such as Los Angeles [_Parrish et al._, 2009]. However, as tighter emission regulations in the US and Europe have led to sharp reductions in transportation VOCs (Figure 1, Past Trend), new sources of pollution have emerged as potentially important precursors to ozone and aerosol formation [_Bahreini et al._, 2012; _Warneke et al._, 2012]. _McDonald et al._ [2018a] have shown that VCPs are a major, under-studied source of urban VOCs that potentially play a significant role in urban air quality and human health. In industrialized cities, VCPs may make up as much as 50% of the total petrochemical VOC emissions and, consequently, could be responsible for as much as 50% of the mass associated with fossil-derived secondary organic aerosol (SOA) formation (Figure 1, Current Inventory).
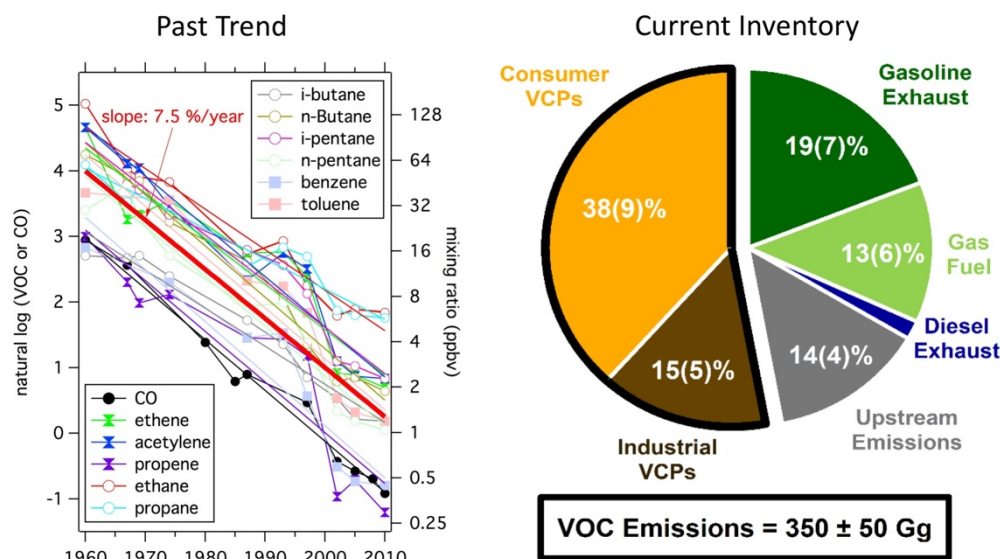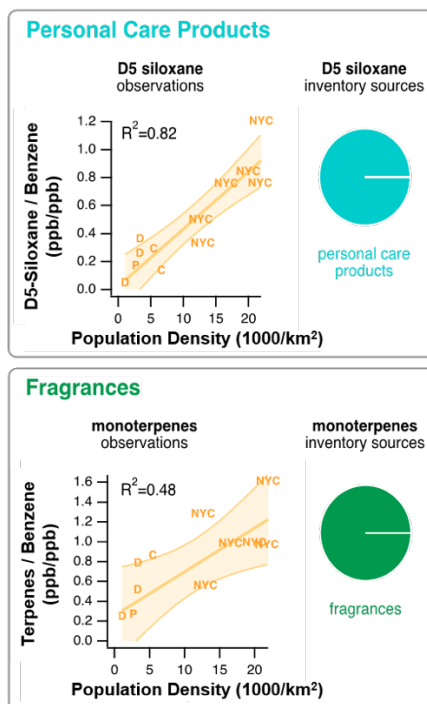
**Figure 1:** (Past Trend) Trends in Los Angeles anthropogenic VOC emissions show sharp decreases in fossil-VOCs observed from 1960 to 2010 [*Warneke et al.*, 2012]. (Current Inventory) Future decreases in fossil-VOCs expected to be slower due to growing influence of VCP emissions [*McDonald et al.*, 2018a]. (8-hour design Value) Trend of 8-hour ozone design value in South Coast Air Basin [data source: South Coast Air Quality Management District RFP P2019-08].

Unlike emissions from vehicles and energy production, VCPs are emitted from a wide range of human activities over a dispersed area. Quantifying the chemical fingerprint and emission strength is challenging. For instance, a significant fraction of VCPs likely originates from use in residential or commercial buildings, and emitted via building exhaust, though it is not well understood what fraction of VCP emissions could also occur outside or at waste facilities (e.g., landfills and wastewater treatment plants). These "indoor" VCPs, which include cleaning and personal care products, constitute approximately 50% of VCP emissions and composed of oxygenated molecules that could form SOA efficiently [*McDonald et al.*, 2018a]. In addition to VCPs, there could be other indoor sources of VOCs from cooking [*Klein et al.*, 2016] and building materials [*Singer et al.*, 2016], and which can contribute primary emissions of reactive aldehydes to the atmosphere.

A recent pilot study in New York City and other major urban areas has shown that there is a clear signature of VCP emissions, such as D5-siloxanes from personal care products and anthropogenic monoterpenes from fragrances in personal care and cleaning products (Figure 2) [*Coggon et al.*, 2020; *M M Coggon et al.*, 2018]. VOCs such as monoterpenes from VCPs might be efficient at producing ozone and SOA in an urban environment. D5 siloxanes and monoterpenes show the largest enhancements in the most densely populated areas around Manhattan and are well correlated with population density. Speciation measurements by GC-MS found that limonene was the dominant monoterpene isomer in downtown NYC during both winter and summer campaigns, which is the most commonly used monoterpene in fragrances, compared to a- and b-pinene from biogenic emissions in New Jersey and Long Island. The monoterpene speciation, the high wintertime mixing ratios, and the correlation with population density clearly prove anthropogenic emissions of monoterpenes, particularly limonene.

**Figure 2:** (NYC Monoterpenes in Winter) The drive track of the NOAA mobile laboratory color-coded with the sum of the monoterpenes measured with PTR-ToF-MS on top of the population density map of the New York City metropolitan area. The pie charts indicate the monoterpene composition determined by GC-MS. (Population Density Dependence of VCPs) The enhancements of D5-siloxane and monoterpenes relative to the traffic marker benzene for U.S. cities with different population densities.

Elevated monoterpene emissions were also measured in other major U.S. cities (Chicago, Denver, and Pittsburgh). Figure 2 shows the ratios of D5 siloxane and monoterpenes to benzene (a marker for vehicle emissions) versus the population density for those cities, where NYC is separated into different areas of the NYC metro area. Emissions from VCPs (D5 siloxane and monoterpenes) are enhanced compared to traffic (benzene) with higher population density, as might be expected, because fewer miles are driven per person at higher populations densities [*Gately et al.*, 2015].
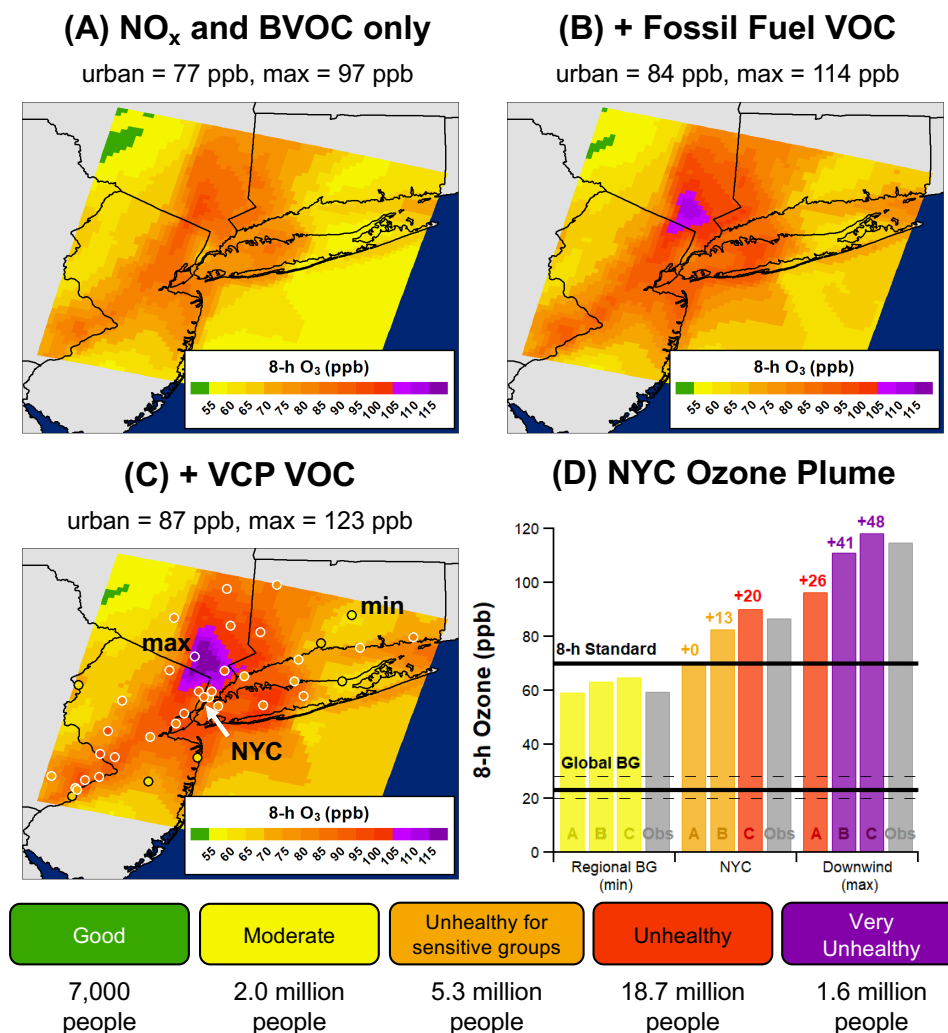
**(A) NOₓ and BVOC only**
urban = 77 ppb, max = 97 ppb

**(B) + Fossil Fuel VOC**
urban = 84 ppb, max = 114 ppb

**(C) + VCP VOC**
urban = 87 ppb, max = 123 ppb

**(D) NYC Ozone Plume**

| Good | Moderate | Unhealthy for sensitive groups | Unhealthy | Very Unhealthy |
|------|----------|-------------------------------|-----------|----------------|
| 7,000 people | 2.0 million people | 5.3 million people | 18.7 million people | 1.6 million people |

**Figure 3:** WRF-Chem simulations of ozone during the July 2, 2018 pollution episode [*Coggon et al.*, 2020]. Shown are simulations for (A) regional ozone background + NOₓ + BVOCs, (B) results from (A) with fossil fuel VOCs included, and (C) results from (B) with VOCs from VCPs added. Circles show ozone mixing ratios measured at monitoring stations in the NYC area; those bolded in white exceeded US air quality standards. The US air quality index, and the populations impacted within each index, are shown for reference. (D) Bar chart summary, color coded by the AQI, of ground site monitors and corresponding WRF-Chem grid cells located in the regional background, NYC center, and ozone maximum downwind of NYC. The numbers above the bars indicate the ozone enhancements above the NAAQS 8-hour standard of 70 ppb.

The VOCs emitted from VCPs play an important role in the production of ozone and SOA as can be seen from VOC data from the pilot study in NYC and other data collected during the LISTOS2018 study (https://www-air.larc.nasa.gov/missions/listos/index.html). On July 2, 2018 an ozone exceedance event occurred in and downwind of NYC, arising from a major heatwave. Figure 3 shows results from a regional chemical transport model, WRF-Chem, simulating this ozone exceedance [*Coggon et al*., 2020]. The model shows that NOₓ and biogenic VOCs contribute ~80 ppb of 8-hour ozone to the urban corridor (panel A), which is enhanced by up to 30 ppb from the addition of anthropogenic VOCs, including from fossil fuel VOCs (panel B) and VCPs (panel C). Ozone levels reached as high as ~120 ppb, which is well in exceedance of the 70 ppb 8-hour ozone

standard, and ~25 million people were exposed to unhealthy air according to the US air quality index (AQI). The same ozone episode was used to initialize a F0AM box model simulation, which was used for a VOC sensitivity study. The box modeling found that fossil fuel VOC emissions are responsible for about 60% and VCPs for almost 40% of the anthropogenic ozone formation related to VOC emissions. The VCP fraction was about evenly split into coatings, cleaning products and personal care products. Ethanol and fragrances were two of the most important VOCs for ozone production during this exceedance event [*Coggon et al.*, 2020].
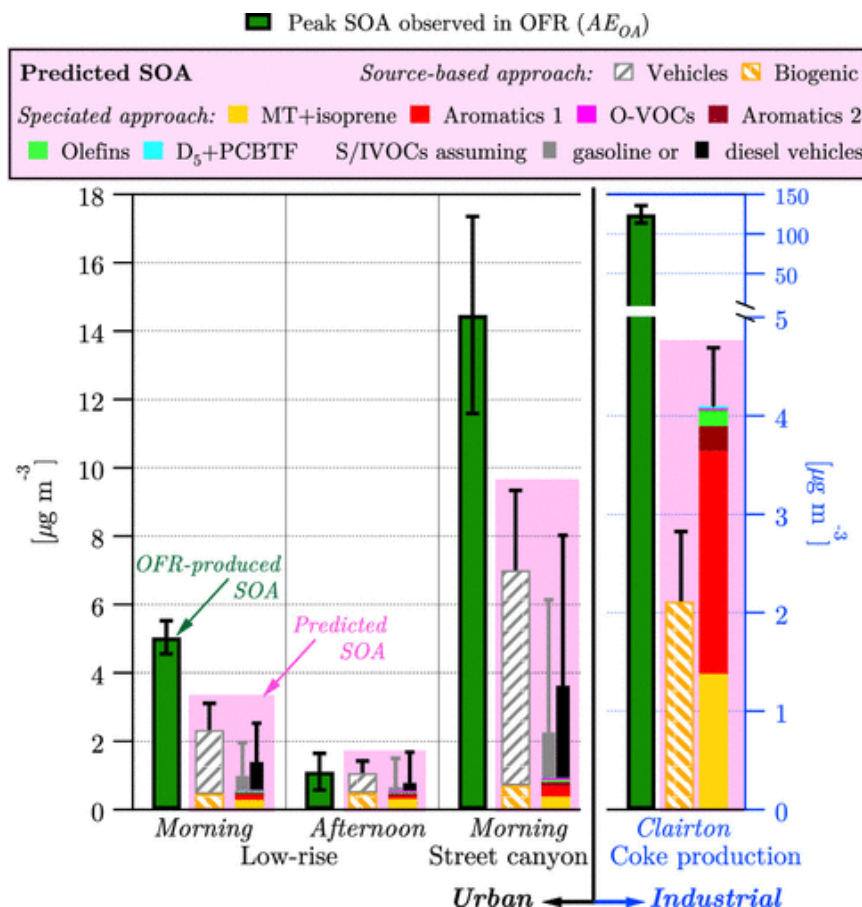


**Figure 4:** Measured and predicted SOA in urban and industrial environments at 2 equivalent days of OH exposure. SOA measured in the OFR is shown by the green bar and predicted SOA based on speciated VOC data by the pink tints. The predicted SOA only accounts for traditional gasoline, diesel and biogenic sources of precursors and under-predicts the observed values by a factor of ~2 and suggesting the influence of VCPs on SOA [*Shah et al.*, 2020].

In addition to contributions to ozone, McDonald et al. [2018a] suggested that VCPs can also contribute to SOA. A recent oxidation flow reactor (OFR) and high-resolution aerosol mass spectrometer (HR-AMS) experiment in New York City and Pittsburgh suggested there are significant SOA contributions from VCPs [*Shah et al.*, 2020]. The study compared the measured SOA from the OFR with predicted SOA formed from mobile sources and biogenics (Figure 4). The measured values were under-predicted by a factor of ~2 when compared with the observed values. The study further investigated what the missing source of urban SOA could be, and performed oxidation experiments on VCP emissions, which revealed that VCPs can efficiently form SOA.

These measurements and models indicate the importance of VCPs, in addition to traditional fossil fuel sources, for ozone and SOA and clearly demonstrate the need for understanding their chemistry in the urban environment and taking VCPs into account in air quality management.

*North American Megacity $NO_x$ Emissions, Chemistry, and Trends*

$NO_x$ is the second needed ingredient for ozone and secondary aerosol formation and has been decreasing since 1960 for example in Los Angeles at a rate of about 2.6% per year [*Pollack et al.*, 2013]. Similar decreases in $NO_2$ are observed nationwide (https://www.epa.gov/air-trends/nitrogen-dioxide-trends) and satellite retrievals of $NO_2$ columns from the Ozone Monitoring Instrument (OMI) indicate a plateau since 2011 (Figure 5, left panel) [*Jiang et al.*, 2018]. A variety of hypotheses have been suggested on why this trend is slowing, including: (i) a decrease in the rate of decline in anthropogenic $NO_x$ emissions [*Jiang et al.*, 2018], (ii) the growing influence of background and free tropospheric $NO_2$ [*Silvern et al.*, 2019], and (iii) changes in $NO_x$ lifetime [*Laughner and Cohen*, 2019].

A recent study suggested that agricultural soils are a dominant source of $NO_x$ pollution in California, with especially high soil $NO_x$ emissions from the state's Central Valley region (Figure 5, right panel). This large, overlooked $NO_x$ source from cropland soil could increase the $NO_x$ budget by 20 to 51% [*Almaraz et al.*, 2018]. Fertilizer application also results in nitrous oxide ($N_2O$) emissions, a potent greenhouse gas, and emissions are strongest in the Midwestern corn/soy belt and in spring/early summer. It is possible that the increasing importance of soil $NO_x$ emissions could be contributing to the slowdown observed in satellite $NO_2$ columns shown in Figure 5, and consistent with NOAA CSL modeling of ozone over the Eastern US, which also suggested an under-accounted soil $NO_x$ source in the Upper Midwest [*McDonald et al.*, 2018b].

In addition to uncertain trends, recent studies have also suggested significant uncertainties in current vehicle emission models of mobile source $NO_x$ based on a variety of field campaigns [*McDonald et al.*, 2018b; *Travis et al.*, 2016]. It is critical to improve inventories of $NO_x$ for accurate model predictions of ozone and aerosol chemistry. With the launch of the Sentinel-5P Tropospheric Ozone Monitoring Instrument (TROPOMI) [*Veefkind et al.*, 2012] and enhanced spatial resolution of its satellite products (3.5 km x 7 km), increasingly satellite $NO_2$ and formaldehyde data are becoming a useful tool for evaluating and constraining emission inventories, including of $NO_x$ [*Beirle et al.*, 2019; *Goldberg et al.*, 2019] and VOCs [*S-W Kim et al.*, 2018]. Satellite capabilities are expected to increase with the anticipated launch of the geostationary Tropospheric Emissions: Monitoring Pollution (TEMPO) satellite in 2022 [*Chance et al.*, 2013].
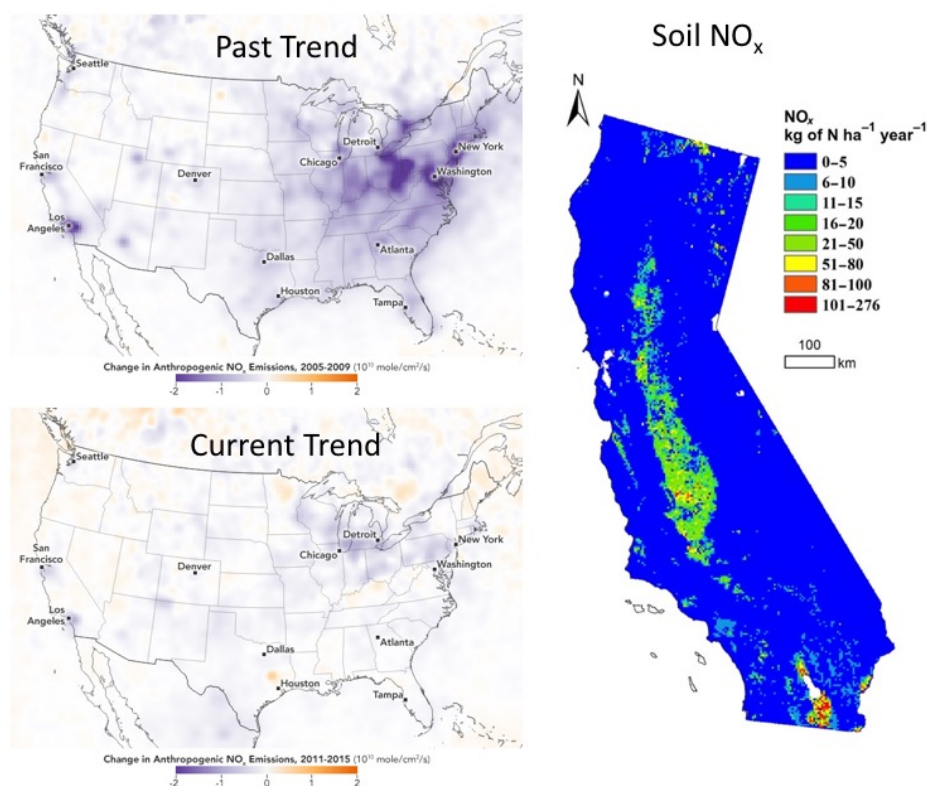
**Figure 5:** Trends in US NOₓ emissions derived from OMI satellite products and utilizing an inverse modeling framework [*Jiang et al.*, 2018]. NOₓ emissions are decreasing from 2005-2009 (Past Trend) but decreases are slowing down from 2011-2015 (Current Trend). (Soil NOₓ) NOₓ emissions from California soils (natural and cropland) generated using stable isotopic modeling and IMAGE model [*Almaraz et al.*, 2018].

## *Tropospheric **Ozone** Formation and Trends*

Overall, summertime levels of tropospheric ozone have been trending downward from 2000-2014 (Figure 6, top panel) [*Gaudel et al*., 2018] together with its precursors as described above. It was also shown recently that ozone maxima decreased in proportion with NOₓ emissions in the southeast US [*Blanchard et al.,* 2018], and there was an observed shift from the NO₂ regeneration product (PAN) to the radical termination product (HNO₃) [*Pollack et al*., 2013]. Prior to the 2008 recession, large emission reductions have been observed from space due to U.S. regulatory efforts to control NOₓ from power plants and transportation [*Tong et al*., 2015].

In contrast to downward trends in average tropospheric ozone levels in North America, the worst days quantified as ozone design values (ODVs) (i.e., the 3-year average of the 4th annual maxima, as regulated under the Clean Air Act) have been decreasing exponentially until recently. If those trends were to continue, it will take ~35 years for the Los Angeles region to be in attainment for ozone [*Parrish et al*., 2017b]. For California, Los Angeles is the air basin with the greatest exceedance of the 8-hour ozone NAAQS in the US, especially in the downwind "Inland Empire" parts of the basin. Currently there are only very few sites in the U.S., where declines in ODVs have slowed from the exponential trend. In the South Coast Air Basin (SOCAB) the progress in the improvement of ozone and PM2.5 concentrations has slowed down in recent years

as can be seen in the increasing trend of the 8-hour ozone design value over the past several years (Figure 6, middle panel). The national trend has also showed a slowdown and is flattening since 2010 (Figure 6, bottom panel). If this trend is caused by changes in $NO_x$ emission sources, or VOCs from VCP emissions, or unusual meteorology associated with the frequency of heatwaves is currently not well understood.
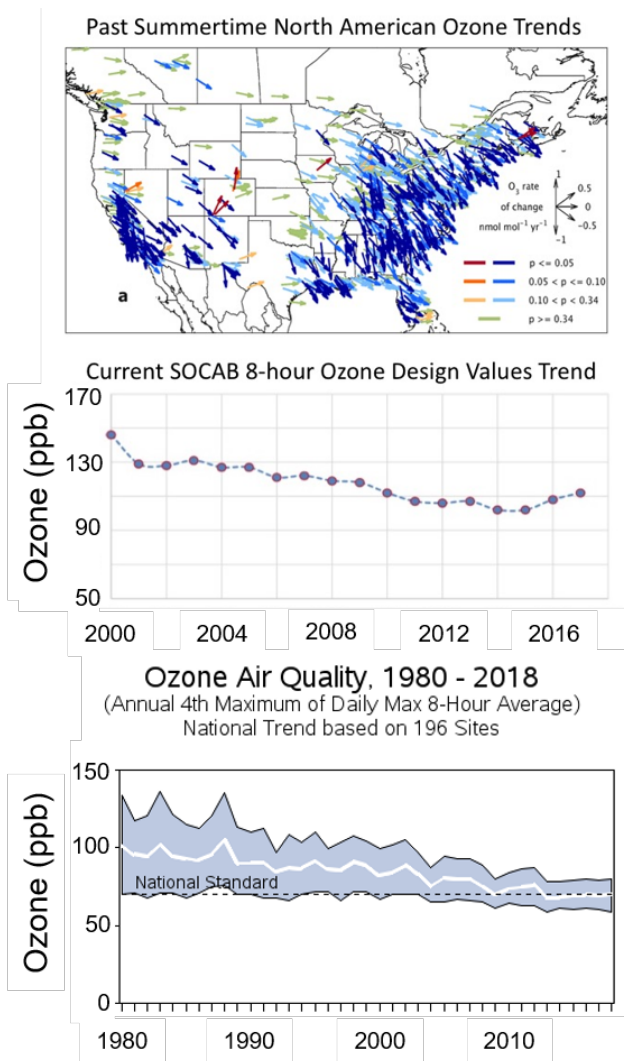


**Figure 6:** (Past Trend) Summertime trends of daytime averaged ozone over North America from 2000-2014 [*Gaudel et al.*, 2018], which have been decreasing overall. (Current SOCAB Ozone Trend) Trend of 8-hour ozone design value in South Coast Air Basin (SOCAB) [data source: South Coast Air Quality Management District RFP P2019-08]. (Ozone Air Quality) National trend based on 196 sites (https://www.epa.gov/air-trends/ozone-trends). Bands show the 10th and 90th percentiles.

*Aerosol Formation and Trends*

Nationally, organic aerosol (OA) comprises around half of the fine particulate matter ($PM_{2.5}$) mass, and US concentrations have been decreasing since 1990. Ridley et al. [2018] attribute the decreases in atmospheric concentrations of OA to reductions in transportation and residential fuel burning emissions, including directly emitted particles and VOC precursors. Similarly, McDonald et al. [2015]found that OA concentrations were decreasing in Los Angeles due to reductions in tailpipe emissions of primary and secondary OA (Figure 7). Although, the decreases were not as large as expected from the observed reductions in mobile source emissions. The study suggested that other VOC sources could be contributing to the slower-than-expected decreases in OA concentrations. McDonald et al., [2018a] later found that the slow OA decrease is likely due to the emerging importance of VCPs.
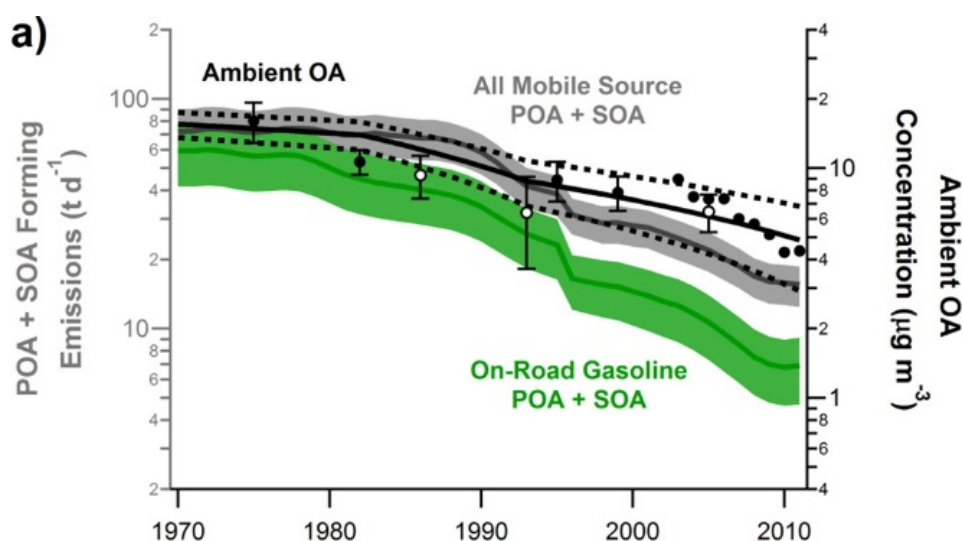


**Figure 7:** Trends in organic aerosol concentrations for the Los Angeles basin [*McDonald et al.*, 2015]. Decreases are attributed to reductions in motor vehicle emissions and other sources of SOA.

Additionally, ammonium nitrate accounted for around ~1/3 of the summertime submicron PM in Los Angeles during CalNex 2010. Heavy-duty diesel trucks have become the leading source of $NO_x$ in the Los Angeles basin [*S W Kim et al.*, 2016], and in cities over the Eastern US [*McDonald et al.*, 2018b]. Starting in 2010, new heavy-duty diesel trucks are required to install selective catalytic reduction (SCR) systems. Under highway driving conditions, the SCR systems are effective at reducing $NO_x$ emissions. However, under urban driving, the SCR systems are ineffective and result in significantly elevated emissions of $NO_x$ [*Dixit et al.*, 2017; *Thiruvengadam et al.*, 2015]. The reagent used to reduce $NO_x$ within the SCR is urea, and if slippage occurs, could also result in a local urban source of ammonia ($NH_3$).

The San Joaquin Valley has the most severe $PM_{2.5}$ problems in the nation, which is also one of the most agriculturally productive regions of the US. In this region, it is expected that aerosol nitrates could form from both precursor emissions of $NH_3$ and $NO_x$ resulting from agriculture. Additionally, the region is a major conduit of interstate long-haul truck traffic. Recently, Womack et al. [2019] suggested that VOCs also play a role in the formation of ammonium nitrate, similar

to how $NO_x$ and VOCs affect ozone chemistry. While Womack et al. investigated wintertime ammonium nitrate formation in Salt Lake City, another modeling study over California [*Zhu et al.*, 2019] found that increasing VCP emissions by a factor of ~3 had non-linear effects on $PM_{2.5}$ via SOA and ammonium nitrate formation. During winter, the CMAQ model predicted increased $PM_{2.5}$ universally across California, mainly through formation of ammonium nitrate from increased VCP emissions. However, in summer, CMAQ predictions of $PM_{2.5}$ were largely unchanged due to increased SOA offset by reduced ammonium nitrate formation from increased VCP emissions. More measurements on the interplay of VOCs, $NO_x$, and $NH_3$ on secondary aerosol chemistry is needed to better predict urban $PM_{2.5}$.

### *Greenhouse Gases and Air Quality Co-Benefits*

Globally, cities account for ~50% of the world population and at least 70% of the $CO_2$ emissions [*Duren and Miller*, 2012]. Yet a robust urban carbon monitoring system for $CO_2$ and $CH_4$ has not been established to track trends in greenhouse gas emissions, though urban testbeds have been established in Indianapolis (INFLUX), Los Angeles (Megacities Carbon Project), and Baltimore/Washington, DC (Northeast Corridor Urban Test Bed) with support from NIST (https://www.nist.gov/topics/greenhouse-gas-measurements/urban-test-beds).

In most US cities, buildings and transportation comprise the two largest sources of $CO_2$ emissions [*Gately and Hutyra*, 2017; *McDonald et al.*, 2014]. These sources also are the two main $NO_x$ sources in cities [*McDonald et al.*, 2018b] and of VOCs to the urban atmosphere [*McDonald et al.*, 2018a] contributing to ozone and $PM_{2.5}$. Fugitive leaks of methane have been shown to occur from the oil and natural gas production and supply infrastructure and landfills [*Alvarez et al.*, 2018; *Kuwayama et al.*, 2019; *Plant et al.*, 2019]. Refineries remain an important source of reactive VOCs [*Johansson et al.*, 2014] and oil and natural gas infrastructure are a source of light alkanes [*Peischl et al.*, 2013]. Relatively little attention has been paid to VOC emissions from landfills, though they could be a potential emission pathway by which VCPs are emitted into the atmosphere. Given the overlap in emission sources that contribute to both air pollutants and greenhouse gases, there are potential synergies for cities to optimize management of air quality and the carbon cycle.

### *The role of **Heatwaves, Meteorology, and Long-Range Transport** on Urban Air Quality*

Over the last 50-60 years, US heatwaves have become more frequent, last longer, and are more intense [*Habeeb et al.*, 2015]. Heatwaves have been associated with enhanced levels of ozone [*Meehl et al.*, 2018], as well as human mortality [*Meehl et al.*, 2018; *Mora et al.*, 2017]. As Figure 3 illustrates for New York City, heatwaves can significantly enhance ozone well in exceedance of national ambient air quality standards [*Coggon et al.*, 2020]. However, the impacts of meteorology on ozone and aerosol formation are complex through dependencies on temperature, sunlight, precipitation, and effects on dynamical and physical processes [*Doherty et al.*, 2017]. For example, warmer temperatures are expected to result in a higher planetary boundary layer which enhances dilution and lowers air pollutant concentrations. This can be offset if a heatwave results in stagnant wind conditions and/or recirculation of air masses that allow for build-up of air pollution.

It is well established from prior NOAA CSL field campaigns that coastal dynamics affect the transport of ozone and other air pollutants, including during NEAQS-2002, ICARTT-2004,

TEXAQS-2000, TEXAQS-2006, and CALNEX-2010 [*Angevine et al.*, 2013; *Angevine et al.*, 2012; *Angevine et al.*, 2006; *Angevine et al.*, 1996; *Banta et al.*, 2011; *Banta et al.*, 2005; *Darby et al.*, 2007; *White et al.*, 2007]. As Figure 8 illustrates, chemical transport modeling from ICARTT2004 shows that ozone can be transported from Washington, DC through New York City up to the Gulf of Maine, which is driven by mesoscale meteorology along the coast [*Lee et al.*, 2011]. There is a lack of high-quality wind profiler and thermodynamic measurements over water surfaces, which inhibits evaluation of numerical weather prediction models [*Banta et al.*, 2018]. Ship or airborne lidars fill a critical measurement gap in providing data that can improve models of the marine boundary layer, land-sea breeze recirculation, vertical mixing, as well as characterizing offshore wind energy resources [*Pichugina et al.*, 2017; *Tucker et al.*, 2009].
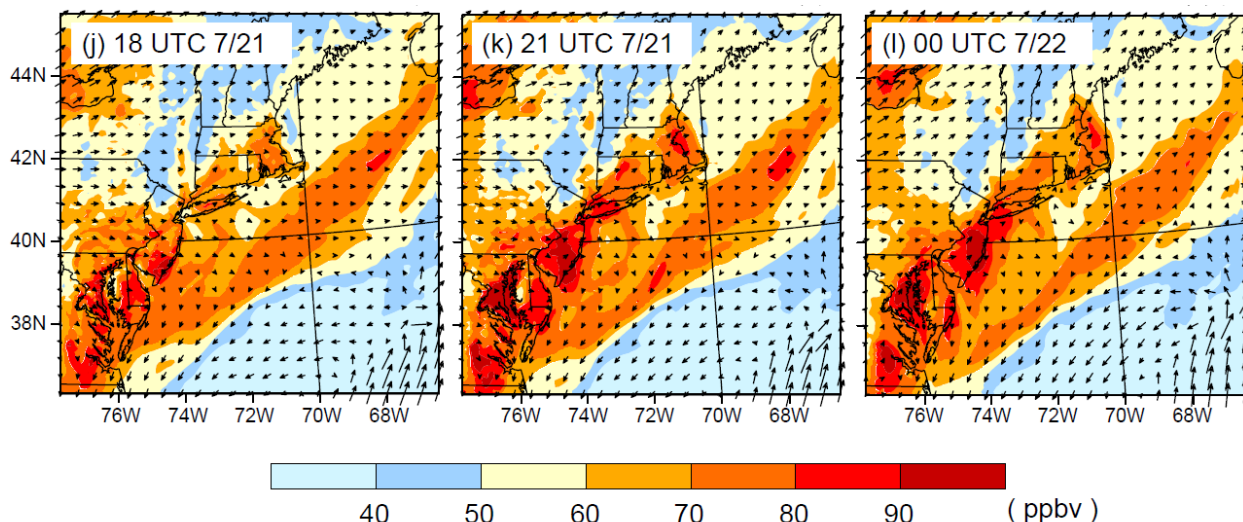


**Figure 8.** Transport of ozone (in ppb) as modeled in WRF-Chem along the US East Coast, from the Mid-Atlantic through the Gulf of Maine, during the ICARTT 2004 field campaign [*Lee et al.*, 2011].

In addition to coastal dynamics, urbanization results in the modification of land surfaces that alter the surface energy balance. Urban heat islands (UHI) result when asphalt or concrete with low albedo replace soils and vegetation and inhibit evapotranspiration. The magnitude of UHI can be modeled as a function of population and precipitation, with the effect stronger in the most populated cities [*Manoli et al.*, 2019]. Accounting for the urban canopy in chemical transport models was shown to improve model predictions of ozone in New York City during the ICARTT 2004 field campaign [*Lee et al.*, 2011]. Using high-resolution vegetation maps and albedo maps was shown to improve the WRF model performance of urban meteorology in Los Angeles [*Vahmani and Ban-Weiss*, 2016]. The effects of urbanization are an additional factor to consider on meteorology in coastal cities. A key question is to what extent does the urban canopy need to be parameterized and represented in chemical transport models? Often the urban canopy is overlooked in operational weather forecasts due to computational cost.

Ozone and aerosols can be transported on regional to continental scales. Global contributions to background ozone are estimated to be ~30 ppb over the Eastern US and have a higher contribution in the Western US of ~40 ppb at high-altitude sites [*Zhang et al.*, 2011]. With the lowering of the 8-hour US ozone standard to 70 ppb, and generally increasing trends of global background ozone [*O. R. Cooper et al.*, 2010], it is becoming more challenging for cities to meet

national ambient air quality standards [*Owen R. Cooper et al.*, 2015]. Additionally, ozone can also be transported from the stratosphere to the troposphere, especially in the intermountain west [*Langford et al.*, 2017; *Langford et al.*, 2015]. Terrain can result in lofting of air pollution from Los Angeles, which lowers concentrations in Los Angeles and elevates pollutants transported over long distances to other states [*Langford et al.*, 2010]. Ozone and aerosol lidars that report vertically-resolved concentrations can be helpful in discerning local versus long-range transport of air pollution, as well as whether there is mixing from the free troposphere to the surface. Figure 9 shows an example of ozone lidar measurements made by the NASA Langley mobile ozone lidar (LMOL) [*De Young et al.*, 2017] located downwind of New York City during LISTOS 2018 [*Coggon et al.*, 2020]. While high ozone levels at the surface are generally decoupled from the free troposphere, there are instances where downward transport of ozone to the surface is evident. Similarly, for aerosols, wildfire smoke from Alberta, Canada has been shown to transport over North America and contribute to increased surface $PM_{2.5}$ by 5-30 µg/m³ in New York City [*Wu et al.*, 2018]. The vertical mixing and transport between the stratosphere, free troposphere, and planetary boundary layer is an additional consideration on coastal meteorology that can affect urban air quality.
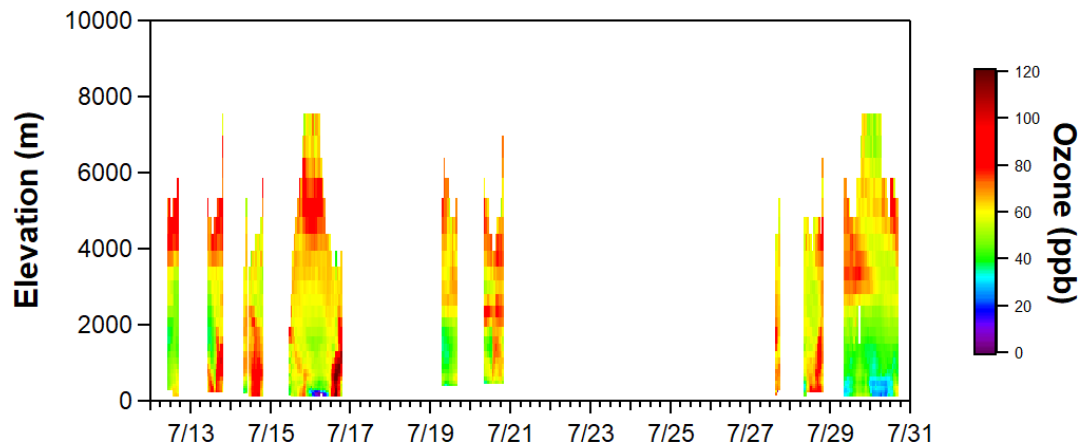


**Figure 9:** Example of ozone lidar measurements by NASA Langley during LISTOS 2018 at Westport, CT.

### *DMS oxidation in the marine atmosphere*

DMS is naturally emitted from the oceans and is the most abundant biological source of sulfur to the marine atmosphere [*Andreae*, 1990; *Andreae et al.*, 1985; *Bates et al.*, 1992]. Once in the atmosphere, DMS undergoes radical-initiated oxidation by hydroxyl (OH), halogen radicals (e.g. chlorine, Cl, and bromine oxide, BrO), and the nitrate radical ($NO_3$) to form a suite of species including $SO_2$ and methane sulfonic acid (MSA, $CH_3SO_3H$), [*Andreae*, 1990; *Andreae et al.*, 1985; *Chen et al.*, 2018; *Hoffmann et al.*, 2016]. Gas phase $SO_2$ can be oxidized further to form sulfuric acid ($H_2SO_4$), a key precursor to new particles formed via homogeneous nucleation in airmasses where the existing condensation sink is small [*Kulmala*, 2003]. These newly formed particles may grow by further condensation and coagulation to sizes large enough to serve as cloud condensation nuclei (CCN), thus affecting cloud optical properties and climate [*Merikanto et al.*, 2009]. In addition, $SO_2$ can partition to aerosol liquid water to form non-sea salt sulfate (nss-$SO_4^{2-}$) [*Boniface et al.*, 2000]. Gas-phase MSA contributes to particle growth via condensation onto existing particles [*Saltzman et al.*, 1983].

Understanding the global impact of DMS in a changing climate and demands that models faithfully represent DMS oxidation chemistry. Yet, parameterizations of the complex DMS oxidation pathways are insufficient to capture how product distributions will respond to physical uptake and varying chemical environments. Studies of DMS oxidation have focused almost exclusively on the yields and fate of the terminal products $SO_2$ and MSA and their impact on the concentration of CCN [*Merikanto et al.*, 2009]. Many of the proposed intermediates in the DMS oxidation scheme have not been directly observed, thus creating uncertainty in the DMS product branching ratios and oxidation timescales. Direct pathways to form sulfate from DMS that bypass $SO_2$ exist, yet remain incompletely understood. The most recent example of such is the identification of hydroperoxymethyl thioformate (HPMTF), a DMS oxidation product, that has been revealed to be a major reservoir of marine sulfur (Fig. 10) [*Veres et al.*, 2019].
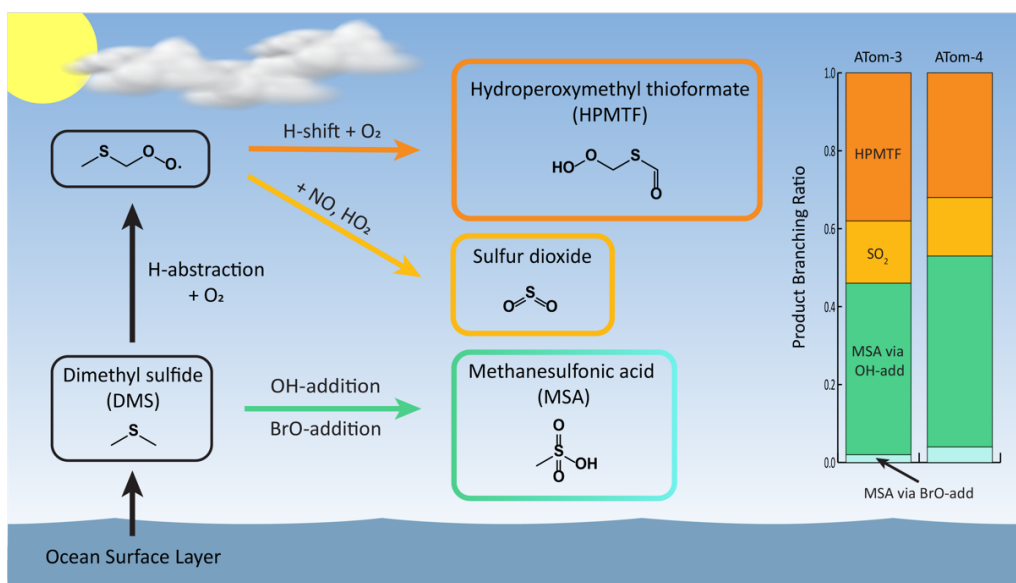


**Figure 10:** Proposed biogenic marine sulfur cycle including HPMTF formation that was recently identified as a dominant DMS oxidation product [*Veres et al.*, 2019].

Accurate representation of both the DMS oxidation product branching fractions and timescales in chemical transport models is critical to establishing a relationship between oceanic DMS emissions, atmospheric particle number and mass, and CCN concentrations in the marine boundary layer (MBL). Understanding the importance of these DMS derived CCN relative to other sources of marine CCN, such as sea-spray aerosol, long-range transport of terrestrial particles, and secondary marine aerosol produced from non-DMS precursors [*O'Dowd and De Leeuw*, 2007; *Prather et al.*, 2013; *Quinn and Bates*, 2011] in both pre-industrial and present-day atmospheres requires complete understanding of the chemical and physical processes affecting DMS oxidation products [*Carslaw et al.*, 2013]. The atmospheric fate of HPMTF, however, remains currently unknown and therefore limits our ability to model the temporal and geographical distribution of the contribution of this newly identified oxidation pathway on global $SO_2$ and sulfate. This lack of knowledge limits our ability to accurately assess the role of DMS in marine sulfur chemistry and its impact on new particle formation and growth, the global distribution of CCN, and their effects on Earth's radiative balance. In current global models, the oxidation of DMS is parameterized to produce $SO_2$ and MSA with fixed yields typically totaling 100%. However, the existence of HPMTF and observations of its solubility demonstrate instead that the majority of DMS oxidation may not result in the formation of gas phase sulfur species at all. If a large fraction of the sulfur emitted from the ocean as DMS is returned to the aqueous phase by uptake onto the sea surface or marine clouds, the availability of condensable gas-phase sulfur will be significantly less than previously thought. This could severely reduce the modeled CCN concentrations in both the present and pre-industrial atmosphere.

*Urban Impact of Marine Halogens*

The marine atmosphere is the main source of natural halogen species (e.g Br, Cl, I) to the atmosphere. Halogenated species, such as $ClNO_2$, are produced through biological and photochemical processes in the marine atmosphere and can release reactive radicals that destroy ozone [*Simpson et al.*, 2015]. Marine halogens can impact the oxidative capacity of the atmosphere by altering $NO_x$ and $HO_x$ budgets [*Alfonso Saiz-Lopez and von Glasow*, 2012]. Previous studies have shown that marine halogens reduce $O_3$ concentrations in marine environments by up to 20% [*A. Saiz-Lopez et al.*, 2012; *Sherwen et al.*, 2016]. Production of $ClNO_2$ on marine aerosols can also result in increases in tropospheric ozone secondary organic aerosol and in coastal urban areas [*Hossaini et al.*, 2016; *Osthoff et al.*, 2008]. A recent modelling study approximates a 10% increase in secondary organic aerosol and reductions in $O_3$ and $NO_x$ in the city of Los Angeles as a result of marine halogen oxidation [*Muñiz-Unamunzaga et al.*, 2018; *Raff et al.*, 2009]. Additional field observations of marine halogen species ($ClNO_2$, $Cl_2$) in coastal urban regions are necessary to further constrain the impact of marine halogens to the budget and balance of the oxidative budget of urban regions, and to assess the role these emissions have on urban air quality in a changing atmosphere.

*Radiative impacts of marine aerosols*

Marine aerosols are produced primarily through three processes: sea-spray, secondary production of sulfate, and secondary production of organics. Marine aerosols can affect the amount of solar radiation reaching the Earth's surface through the production of CCN (Figure 11). The remote marine atmosphere is particularly sensitive to the production of additional CCN due to the low concentrations of CCN in this environment. Production of CCN can dramatically change the number and size of cloud droplets [*Andreae and Rosenfeld*, 2008; *Moore et al.*, 2013]. One study

in particular observed a doubling in the cloud droplet number concentration as a result of a marine aerosol production associated with a phytoplankton bloom in the Southern Ocean resulting in a calculated change in the local radiative flux of -15 W m$^2$ [*Meskhidze and Nenes*, 2006]. These indirect effects of marine aerosols on clouds remains the largest uncertainty in current IPCC radiative forcing estimates. Therefore, parameterization of the sources of these aerosols is important to understanding changes in Earth's radiation balance as a result of changes in the burden and properties of these aerosols as a result of a changing climate. In-situ atmospheric measurements with high spatial resolution of MBL aerosol loading and microphysical properties, effects of cloud processing and entrainment of aerosols from the free troposphere and non-sea- salt sulfate, are required are required to improve parameterization of ocean ecosystem-CCN-cloud for Earth system models.
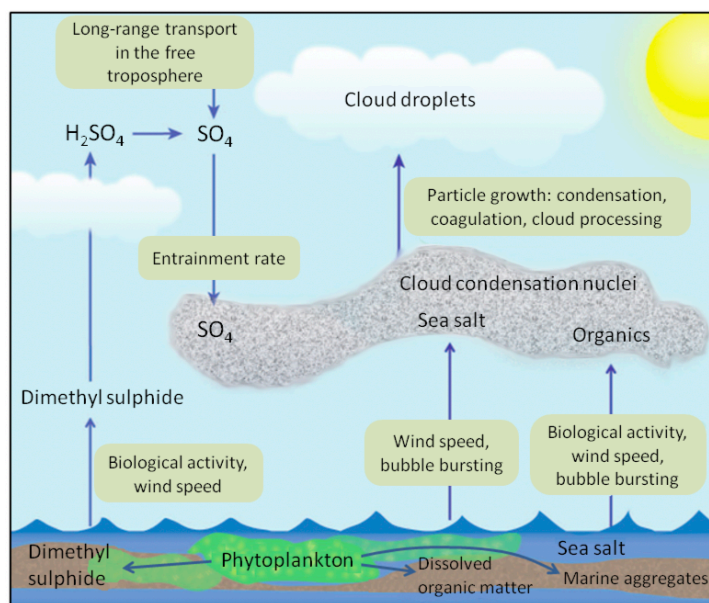


**Figure 11:** Linkages between air-sea exchange and the production the production of CCN in the remote marine atmosphere [*Quinn and Bates*, 2011]**.**

*Source Apportionment of sulfur emissions*

Although direct anthropogenic emissions of SO$_2$ currently dominate indirect biogenic sources on a global scale, natural DMS emissions may have a more important impact on global climate. Anthropogenic SO$_2$ emissions originate primarily from northern midlatitude continental point sources, and the atmospheric lifetime of approximately a few days limits its global impact. DMS on the other hand, is emitted over vast regions of Earth's oceans, and is the main source of particulate sulfate over the majority of the tropical marine boundary layer. These particles in turn play an important role in controlling the albedo of tropical marine cumulus clouds. Global anthropogenic SO$_2$ is expected to continue to decrease as a result of emissions regulation [*Klimont et al.*, 2013; *Krotkov et al.*, 2016], while emissions of DMS continue to increase in a warming climate [*Galí et al.*, 2019; *Grandey and Wang*, 2015], further increasing the relative impact of the DMS fraction of global reactive sulfur in the future.

Globally, the most important source region for new particles is thought to be the tropical free and upper troposphere (UT) [*Williamson et al.*, 2019]. Trace gases in this region are primarily transported there via intense tropical deep convection, bringing air from the marine boundary layer into the UT. The small amount of $SO_2$ in this region which is a key ingredient for new particle formation is therefore most likely sourced from oxidation of DMS. Understanding the $SO_2$ yield from DMS oxidation is therefore key to understanding the availability of $SO_2$ for UT aerosol nucleation and growth.

Oxidation of DMS is also thought to result in a very minor (0.7% mol / mol) yield of carbonyl sulfide (OCS). This however small yield is nonetheless presently calculated to be the single largest source of OCS to the global atmosphere [*Kettle et al.*, 2002]. OCS is a key climate gas through its role as the dominant source of aerosol mass in the stratosphere under non-volcanic conditions [*Bruehl et al.*, 2012]. Understanding trends in climate and changes since pre-industrial require accurate estimates of the trends in OCS and therefore stratospheric albedo. The 0.7% yield is at present is derived by a single laboratory study, and it has not been possible to support this yield by e.g. a field study with accurate closure of the sulfur budget.

**Proposed Experimental Plan for NOAA WP-3**

*Location*

To meet the overall AEROMMA 2021 science objectives the NOAA WP-3D aircraft will be deployed to **Ontario, CA and Portsmouth, NH from approximately June 1 to July 31, 2021**.

**Ontario, CA** will provide the WP-3D access to the urban areas of Los Angeles together with regions where DMS chemistry is known to be active of the coast of Los Angeles and the Salton Sea, where high DMS and halogen emissions have previously been observed. From Ontario, CA flight plans will be developed to sample the Los Angeles urban center and conduct sampling throughout the gradient between urban and marine atmosphere in a single flight. The close proximity of Ontario, CA to marine environments with limited anthropogenic influence limits the loss of flight hours due to transit times. Elevated marine sulfur chemistry in coastal areas is a common feature globally and was validated during an AEROMMA concept flight performed during FIREX-AQ project in September 2019, where HPMTF mixing ratios ranged 100 - 300 ppt immediately off the coast of the LA basin. Flights in these regions additionally provide the opportunity to identify the impacts from neighboring agricultural influences in the California Central Valley. On the transit from Florida to California, Houston could be investigated.

From **Portsmouth, NH** the WP-3D can survey all the major urban areas on the east coast such as New York, Chicago, and Toronto, together with the agriculture in Wisconsin, Iowa and Illinois. Deployment in the Northeastern US provides the ability to access regions in the Northern Atlantic which are highly impacted by DMS oxidation chemistry (Figure 12). Anthropogenic outflow on the Eastern coast of the US provides ideal conditions to study the composition and aging of urban emission at the interface of marine environments. The TROPOMI monthly average $NO_2$ map in Figure 12 clearly shows the large urban areas, but also regions with low NOx and strong NOx gradients of the east and west coast within the study region overlapping with high seawater DMS concentrations making for ideal conditions to study the transition from isomerization chemistry forming HPMTF to bimolecular NO chemistry forming $SO_2$.

To support the overall AEROMMA 2021 science objectives related to coastal meteorology the NOAA Twin Otter aircraft will be deployed to the **New York City region from approximately June 1 to July 15, 2021**.

The Twin Otter will study diurnal forcing of atmospheric dynamics on urban plume transport and mixing in coastal regions. Atmospheric effects such as the urban heat island and complex regional flow driven by sea/land breezes have a strong diurnal signature and impact the depth to which urban emission mix in the boundary layer and the coherence and direction of low-level transport in coastal regions. If these processes are not properly represented in regional air quality models, they will not accurately predict air quality in the region. An airborne scanning Doppler lidar will be used to make profile measurements of horizontal wind speed and vertical turbulence and mixing with sufficient resolution to characterize variations in these quantities over regional/urban scales represented by these models. Model performance will be evaluated by tracking the temporal and spatial evolution of the urban plume downwind of major northeast corridor urban centers (Baltimore/Washington, NYC, and Boston). Airborne, in-situ, gas phase concentrations of CO, $CO_2$, $O_3$, $H_2O$, $CH_4$ will be made to aid in air mass identification and to

characterize the spatial extent of the plume. The airborne measurements will be augmented with those made by scanning Doppler lidars deployed in the area of study and greenhouse gas concentrations monitored by the NIST Greenhouse Gas Measurement Testbed and Mole Fraction Measurement Network - Northeast Corridor-Baltimore/Washington (NEC/BW).

*Flight Allocations*

AEROMMA 2021 will require 160 NOAA WP-3D flight hours, which includes test and transit flights and approximately 21 science flights. We anticipate conducting 2-3 flights for the major Megacity targets covering weekday/weekend, urban/rural gradients, and diurnal cycles and half a flight each for the Central Valley and the agricultural areas in the upper Midwest totaling 13 flights. Depending on meteorological conditions each flight to a megacity can cover other smaller cities or more than one megacity. Two flights in Los Angeles and the Central Valley were already conducted during FIREX-AQ in 2019.

We estimate six NOAA WP-3D flights dedicated to survey of the marine atmosphere and the urban interface between Ontario and Portsmouth. Both east and west coast regions have variable NOx mixing ratios, temperature, background aerosol, and cloud properties that are accessible throughout the flight range of the NOAA WP-3D to provide the necessary statistics for studying the impact of these parameters on the distribution and fate of marine emissions, oxidation chemistry and aerosol abundance and composition.

AEROMMA 2021 will require 175 NOAA Twin Otter flight hour and approximately 22 science flights. Flights are anticipated every other day to target coastal dynamics and urban plumes along the Northeast Corridor, and to provide necessary statistics to improve NOAA weather-chemistry model predictions of coastal meteorology and urban plumes of gas-phase species. The Twin Otter will be based in the Northeast US during the field campaign.
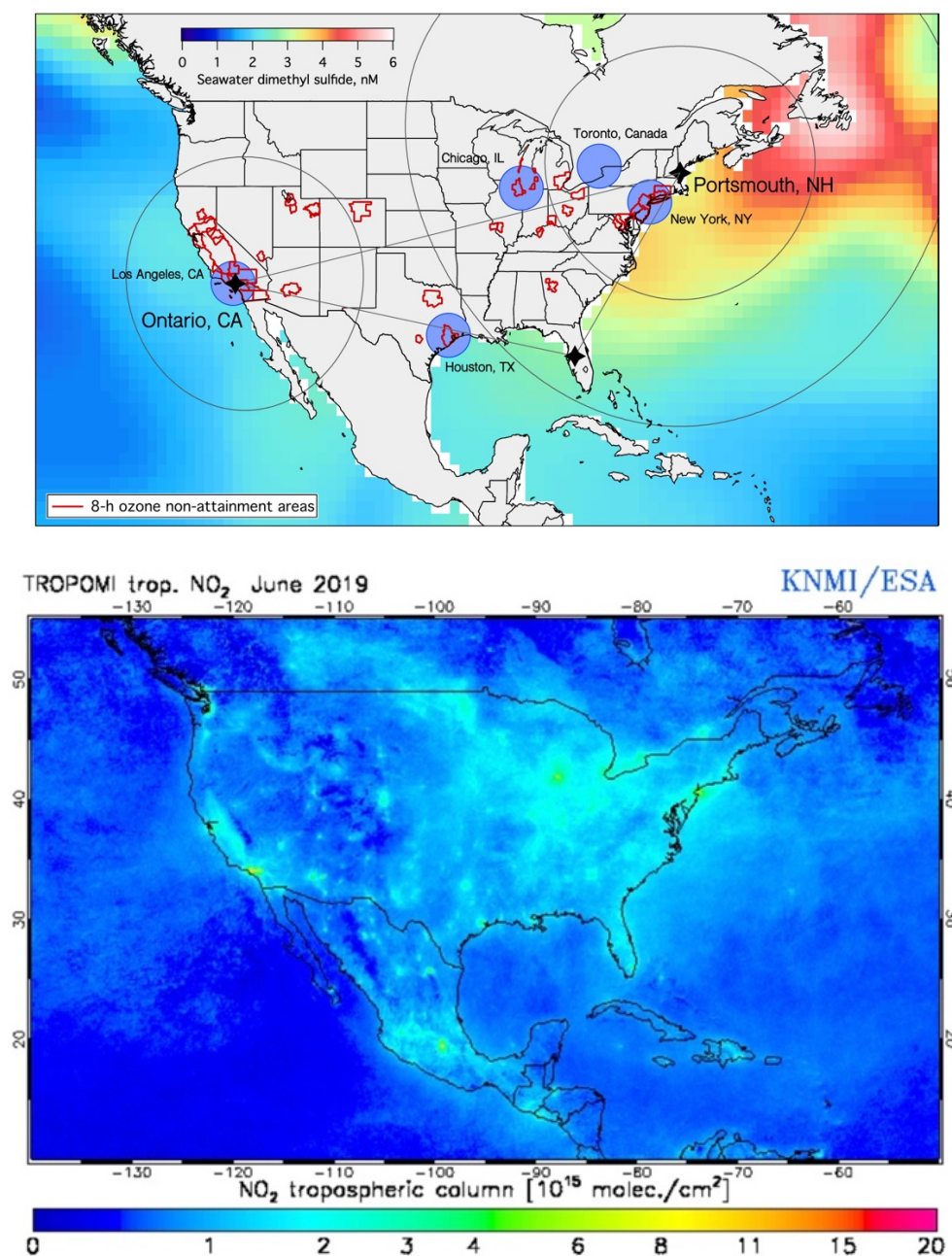
**Figure 12:** (top) The range of the NOAA WP-3D aircraft flying out of Ontario, CA and Portsmouth, NH. (bottom) TROPOMI NO₂ June 2019 monthly mean.

### Study Period

We propose mid-May to mid-July as the study period to deconflict with hurricane season and to cover the maximum ozone occurrence, which is shifting earlier into the summer season since the 1970s as shown in Figure 13 [*Parrish et al.*, 2017a]. This time period also has a high probability of being impacted by the presence of clouds allowing for observations of aqueous oxidation and cloud processing of marine sulfur.
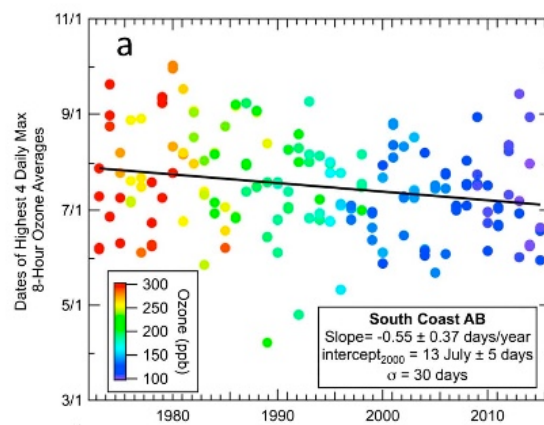
**Figure 13:** Evolution of the dates of occurrence of the highest maximum daily 8 h ozone design values.

*Proposed Payload*

The payload shown in Figure 14 is capable of answering all the major science question for AEROMMA 2021. We propose to equip the NOAA WP-3 aircraft with instruments that have a high enough sampling frequency to be able to do wavelet eddy covariance flux measurements to determine emissions and deposition of for urban VOCs, $NO_x$, CO, $CO_2$, and $CH_4$. A high-resolution aerosol mass spectrometer is needed to quantify the aerosol composition, including the formation of secondary organic aerosol. High-resolution measurements of ethane can help separate fossil and non-fossil components of $CH_4$ [*Peischl et al.*, 2013].
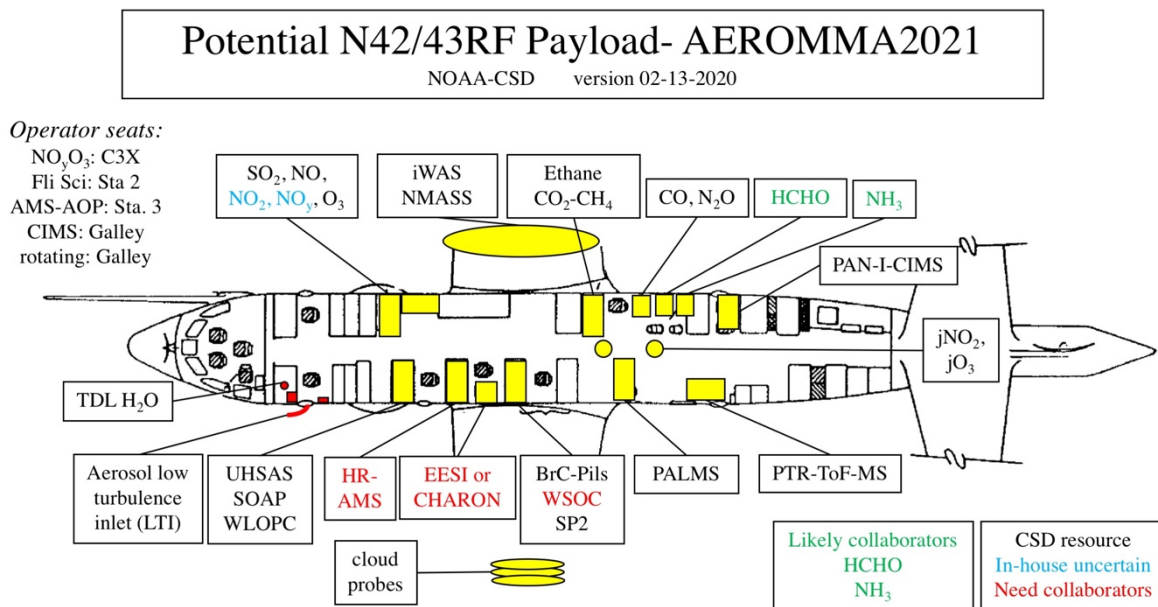


**Figure 14:** Potential payload for the NOAA WP-3 aircraft for MAQS-SORCIRI 2021.

**Related Activities**

*Potential stakeholders in state and regional organizations*
      California: ARB, SCAQMD
      Midwest: LADCO
      Northeast US: NESCAUM, NYSERDA
      Texas: TCEQ
      Canada: ECCC, Univ. Of Toronto

*Other federal agencies*
      NIST Greenhouse Gas Measurements Program
      NOAA Global Monitoring Laboratory
      NOAA Global Systems Laboratory
      EPA Office of Research and Development
      EPA Office of Air Quality Planning and Standards
      NASA Tropospheric Composition Program

*Previous experiments in the study region with CSL involvement*
      TEXAQS2000
      NEAQS2002
      ICARTT2004
      TEXAQS2006
      CalNEX2010
      WINTER2015
      NY-ICE/LISTOS2018
      FIREX-AQ2019 transit flights

*Current plans from other partners*
      New York LISTOS2020/21
      Toronto2021
      NSF GOTHAMM2021 (pending)
      DOE TRACER2021-22

*Remote sensing*
      Airborne Hyperspectral Imaging of VCPs
      NASA GeoTASO/GCAS

*Laboratory experiments in preparation for AEROMMA 2021*
- tracking VCP/cooking/building emissions from gas to particle phase
- Gas-phase chemical mechanisms for understudied oxyVOCs from VCPs

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